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A mathematical and empirical model of the performance of a membrane-coupled anaerobic fermentor

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Abstract A mathematical model was developed to describe the performance of a membrane-coupled anaerobic fermentor (MCAF)-based process. In our experimental results, higher volatile fatty acid (VFA) recovery ratios were obtained at greater filtration ratios. The VFA recovery ratio peaked at an HRT of 12 h and a membrane filtration ratio of 0.95 at a constant SRT. Based on our simulation, the HRT and filtration ratio should be maintained at less than 1 day and above 0.9, respectively, to exceed an organic materials recovery ratio of 35% at a constant SRT of 10 days. Our empirical model, which predicts the effluent VFA concentration (C_o), described the performance of the MCAF adequately. The model demonstrated that the outlet VFA concentration was a function of three independent parameters—HLR, input organic concentration (C_i), and membrane filtration ratio (ϕ). Multiple regression analyses were conducted using 50 measurements of the MCAF, yielding the following relationship: $C_o = 0.278\phi^{1.13} C_i^{1.93}$ HLR$^{0.11}$. The correlation coefficient (R^2) was 0.90. The simulation results were consistent with the observed data; therefore, due to its simplicity, this model predicts the effluent VFA concentration of an MCAF adequately.

Keywords Empirical model · Mathematical model · Membrane-coupled anaerobic fermentor · VFAs

Abbreviations

ε	VFAs consumption ratio by aeration
ϕ	Membrane filtration ratio
C_1	Degradable solids or polymer organic materials (mg C/l)
C_2	Dissolved organic materials (hydrolysis unnecessary) (mg C/l)
C_3	Volatile fatty acids (VFA) (mg C/l)
C_i	Input organic concentration (g C/l)
C_o	Effluent VFA concentration (g C/l)
C_r	Refractory organic concentration (mg C/l)
F_1	Membrane passage ratio of C_1
F_2	Membrane passage ratio of C_r
G	Gasification and mineralization ratio (%)
G_1	Mineralization ratio from C_1 (%)
G_2	Mineralization ratio from C_2 (%)
HLR	Hydraulic loading rate (l/l day)
HRT	Hydraulic retention time (day)
k_1	Hydrolysis rate coefficient (1/h)
k_2	Acid-forming rate coefficient (1/h)
k_3	VFAs consumption rate coefficient (1/h)
k_d	Self-degradation rate coefficient for acid-forming bacteria (1/h)

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M	Hydrolysis by acid-forming bacteria (mg C/l)
OLR	Organic loading rate (kg C/m^3 day)
ORP	Oxidation–reduction potential (mV)
Q	Input discharge (l/h)
Q_1	Permeate flow rate (l/h)
R_1	Hydrolysis rate (mg C/l h)
S_e	Organic concentration in effluent (mg C/l)
S_i	Organic concentration in influent (mg C/l)
SRT	Solids retention time (day)
V	Bioreactor volume (l)
VFA	Volatile fatty acids (mg C/l)
Y_1	Yield coefficient from C_1
Y_2	Yield coefficient from C_2
α	Yield coefficients from C_1 to C_2
β	Yield coefficients from C_2 to C_3
γ	Yield coefficients from C_1 to C_r
γ_m	Yield coefficients from M to C_r
δ	Yield coefficients from M to C_1

Introduction

The acid phase is viewed as two reactions that occur in series. In the first reaction, degradable solids are hydrolyzed to smaller soluble molecules. In the second reaction, acid-forming bacteria use these soluble intermediates as substrates for energy and growth, resulting in the generation of fermentation products and cellular material. Cellular decay or endogenous metabolism is assumed to contribute to the pool of fermentation products (Eastman and Ferguson 1981). These phases represent a key period of biochemical activity in a membrane-coupled anaerobic fermentor (MCAF). The dynamic balance between them is essential for the rate acidogenesis to peak.

To identify reliable design conditions of the MCAF and assess its performance, we need an appropriate mathematical model. Knowledge of the rate-limiting biochemical reaction is important when monitoring or predicting the performance of an MCAF. Several mathematical models have been proposed to define the performance of anaerobic treatment processes. Although many dynamic and steady-state models have been developed to describe the behavior of anaerobic processes, few models have incorporated the kinetics of MCAF-based processes with regard to the recovery of organic materials. No model has been developed sufficiently to evaluate effluent VFA concentrations and the influence of other operational parameters satisfactorily.

There are differences between our model and existing models. First, we made coagulated sludge a target of our model, but existing models have focused on synthetic wastewater or specific wastewater. Second, the model that we developed in this study predicts the performance of the MCAF in recovering high levels of VFAs as byproducts during the fermentation of coagulated sludge. Other models, however, have sought to evaluate the performance of anaerobic reactors that remove organic compounds. Finally, the models differ with regard to the limitations of parameters. Because existing models have used only hydraulic retention time (HRT) in anaerobic treatment and have not considered membrane filtration, they are unable to predict the performance of MCAFs.

Moreover, the complexity, uneven distribution of anaerobic biofilms in the reactors, and interactions between microbial species complicate any attempt at modeling such a process. The complexity of anaerobic biotransformation reactions increases significantly when organic substrates that require hydrolysis and fermentation are added to the system. Due to the complexity and difficulty in representing MCAF-based processes with a mathematical model, most existing models are simplifications of the actual system (Dinopoulou et al. 1988). Therefore, the development of an empirical model is necessary to predict effluent VFA concentrations under practical operational conditions. Also, simple empirical models of biological processes can minimize the extensive analysis of complex experimental data.

The primary purpose of this study was to develop an appropriate mathematical model with regard to the operational parameters—such as hydraulic retention time (HRT), solids retention time (SRT), membrane filtration ratio (ϕ), hydrolysis rate constant (k_1), and refractory material ratio (C_{r0}/C_{T0})—that are the predominant variables in determining organic compound recovery and conversion ratios. The secondary objective was to establish an empirical model, based on multiple regression analysis, to predict effluent VFA concentrations in terms of HRT, hydraulic loading rate (HLR), input organic materials

concentration (C_i), and membrane filtration ratio (ϕ) in an MCAF-based process.

Modeling approach

Overview of mathematical acidogenic phase model

Many authors have modeled fermentation processes over the past 15 years. Conceptually, the anaerobic digestion of complex organics can be described as a three-stage process, comprising: (1) hydrolysis, liquefaction, and fermentation; (2) hydrogen and acetic acid formation; and (3) methane generation. Five groups of bacteria (fermentative bacteria; hydrogen-producing, acetogenic bacteria; hydrogen-consuming, acetogenic bacteria; CO_2-reducing methanogens; and aceticlastic methanogens) are believed to participate, each deriving energy from a limited number of biochemical reactions (Parkin and Owen 1986).

There are many mathematical models of the anaerobic treatment of sewage or wastewater, such as performance curve fits (Young and Dahab 1983), mechanistic models (Bhadra et al. 1984; Lindgren 1983), steady-state models (Hanaki and Matsuo 1985; Mosey 1983), and dynamic models that incorporate measurements of substrate diffusion through biofilm (Annachhatre and Khanna 1990; Williamson and McCarty 1976; Suidan and Wang 1985). These models assume operation, ideally, in a continuously stirred tank reactor (CSTR) or under plug-flow conditions. Harper and Suidan (1991), McCarty and Mosey (1991), and Pavlostathis and Girlado-Gomez (1991) have published comprehensive reviews of models of anaerobic digestion methods, including the use of anaerobic filters.

Most models describe growth merely as an increase in biomass or as simplistic microbial conversion reactions but fail to describe changes in microbial distribution. Bryers (1985) structured models to consider mixed-culture population dynamics and multiple reaction schemes as a function of environmental conditions. Hayes et al. (1990) proposed a chemical equilibrium model to describe the steady-state condition of digesters. Bill et al. (1995) developed an equilibrium model to study the physical and chemical aspects of anaerobic fixed-bed biofilm reactors.

Due to the wide variety of biodegradable materials in sewage sludge, no simple equation or rate constant can describe the rate of biodegradation in waste degradation adequately (Pavlostathis and Gossett 1996; EL-Fadel et al. 1996). Certain substances, such as sugars and starches, are readily decomposable, whereas others, such as cellulose and lignin, require longer times to decompose.

Anaerobic digestion is divided into three phases: hydrolysis, an acidogenic reaction, and a methanogenic reaction. Much research has been conducted concerning the properties of substrate degradation and microbial growth. Today, in anaerobic fermentation processes for sewage sludge that contains primarily insoluble organic particulates, the acidogenic phase, rather than the methanogenic phase, is generally considered the rate-limiting step. To this end, research on the hydrolysis kinetics of solid materials during anaerobic digestion has been performed (Kim and Somiya 1995).

The practical application of such models, however, relies on several assumptions, many of which are not supported by adequate quantitative data. The precision and accuracy of the predictions are affected by uncertainties in the input data. There are no reliable methods of estimation, such as mathematical models, to predict the unknown performance of processes (Kim 1997).

Model description

The basic assumption was as follows: in a closed system, the rate of growth of bacteria and consumption of substrate are proportional to the number of living organisms. In a continuous culture of an MCAF, we also assumed that substrate was added to the fermentor at the input organic concentration (C_{T0}) and flow rate (Q) while its volume (V) was held constant by extracting the solution at the same flow rate ($Q_1 + Q_2$) (Q_1: permeate flow rate, Q_2: bleed flow rate). The transformation of organic materials in the reactor is shown in Fig. 1a, and the flow of discharge is shown in Fig. 1b.

The transformation paths of input organic materials into the MCAF were assumed as follows. Initially, degradable particles or polymer organic matter (C_1) is hydrolyzed by VFA-forming bacteria into a mixture of acid-forming bacteria (M), inert organic materials (C_r), and CO_2. If an environmental condition is fixed, the hydrolysis rate of organic materials is a first-order

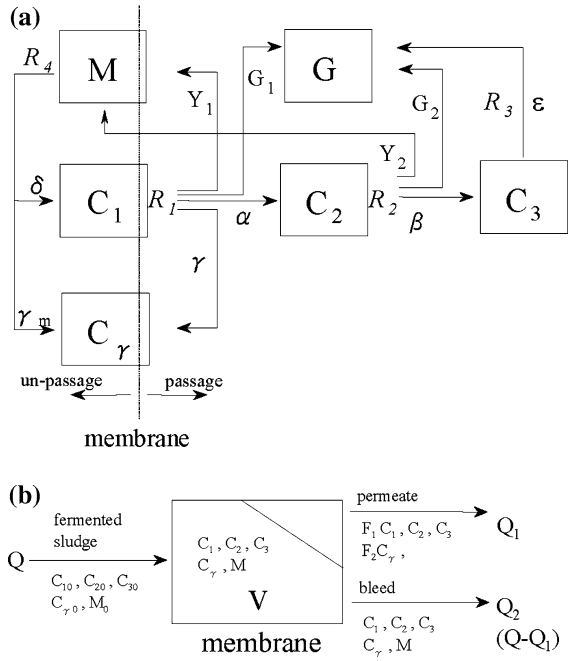

Fig. 1 **a** State variables and transformation paths and **b** flow of discharge and organic materials in the MCAF-based process

reaction with regard to the remaining degradable solid matter. This equation can be expressed as:

$$R_1 = -\frac{dC_1}{dt} = k_1 C_1 \tag{1}$$

Then, the hydrolyzed, dissolved organic materials (C_2) are finally transformed into VFAs (C_3) by acid-forming bacteria. Degradable solids or polymer organic materials (C_1) become dissolved organic materials (C_2), acid-forming bacteria (M), inert organic materials (C_r), and CO_2 (G), depending on yield coefficients (α, Y_1, γ and G_1). Then, the sum of α, Y_1, γ, and G_1 equals 1.

Also, the dissolved organic materials (C_2) become volatile fatty acids (C_3), acid-forming bacteria (M), and CO_2 (G), depending on yield coefficients (β, Y_2 and G_2). $\beta + Y_2 + G_2$ equals 1. Moreover, this mathematical model also considers VFA consumption by intermittent aeration in the reactor, based on Ağdağ and Sponza's experimental results (Ağdağ and Sponza 2005)—i.e., the VFAs that are produced are decomposed slightly by intermittent aeration. O'Keefe et al. (2000) reported a sudden decrease in the production of VFAs after short-term aeration due to the immediate metabolization of VFAs that were produced by facultative bacteria.

In contrast, acid-forming bacteria can self-decompose and become degradable solids or polymer organic materials (C_1) and recalcitrant organic materials (C_r), depending on yield coefficients (δ and γ_m). C_1 and C_r are supposed to pass the membrane, according to F_1 and F_2, where $0 \leq F_i \leq 1$.

To simplify the development of a mathematical model for MCAF-based processes, the following assumptions were made:

(1) The fermentor was mixed completely.
(2) CO_2 and H_2 were the only gaseous end products of anaerobic organic acid fermentation.
(3) The effect of microbial distribution did not consider the transformation or consumption of organic materials.
(4) Microbes did not leak through the membrane.

Based on these assumptions, the mass balance of each step was established to determine the kinetic rate coefficients and unknown variable values in differential equations. The mass balance equations for each state variable of the MCAF process can be written as follows:

$$C_1: V\frac{dC_1}{dt} = QC_{10} - (Q - Q_1)C_1 - F_1Q_1C_1 - k_1C_1V + \delta k_d MV \tag{2}$$

$$C_2: V\frac{dC_2}{dt} = QC_{20} - QC_2 - k_2C_2V + \alpha k_1C_1V \tag{3}$$

$$C_3: V\frac{dC_3}{dt} = QC_{30} - QC_3 + \beta k_2C_2V - \varepsilon k_3C_3V \tag{4}$$

$$C_r: V\frac{dC_r}{dt} = QC_{r0} - (Q - Q_1)C_r - F_2Q_1C_r + \gamma k_1C_1V + \gamma_m k_d MV \tag{5}$$

$$M: V\frac{dM}{dt} = QM_0 - (Q - Q_1)M + Y_1k_1C_1V + Y_2k_2C_2V - k_dMV \tag{6}$$

$$G: V\frac{dG}{dt} = V(1 - \alpha - Y_1 - \gamma)k_1C_1 + V(1 - \beta - Y_2)k_2C_2 + \varepsilon k_3C_3V \tag{7}$$

Simulation conditions

All parameters and operating conditions for the model calculation are listed in Tables 1, 2, and 3.

Table 1 Transformation rate of each state variable

State variable	Unit	Symbol	R_1 (mg C/l h)	R_2 (mg C/l h)	R_3 (mg C/l h)	R_4 (mg C/l h)
Degradable solid or polymer organic materials	mg C/l	C_1	$-R_1$			$R_4\delta$
Dissolved organic materials	mg C/l	C_2	$R_1\alpha$	$-R_2$		
Volatile fatty acids	mg C/l	C_3		$R_2\beta$	$-R_3$	
Recalcitrant organic materials	mg C/l	C_r	$R_1\gamma$			$R_4\gamma_m$
Hydrolysis acid-forming bacteria	mg C/l	M	R_1Y_1	$R_2\ Y_2$		$-R_4$
Mineralization and gasification	mg C/l	G	$R_1(1-\alpha-\gamma-Y_1)$	$R_2(1-\beta-Y_2)$	$R_3\varepsilon$	
Sum			0	0	$-R_3(1-\varepsilon)$	$R_4(1-\delta-\gamma_m)$

Table 2 Rate constants and coefficients

Parameter	Unit	Selected value	The range of other reference[a,b,c,d]
k_1	1/h	0.0122	0.0001–0.225
k_2	1/h	0.1916	0.0001–0.256
k_3	1/h	0.0174	0.00675–0.37
k_d	1/h	0.0015	0.0015–0.005
α	–	0.85	–
β	–	0.75	–
γ	–	0.01	–
γ_m	–	0.7	–
δ	–	0.3	–
ε	–	0.03	–
Y_1	–	0.01[b,c]	0.005–0.035
Y_2	–	0.022[b,c]	
F_1	–	0.04[b,c]	–
F_2	–	0.02[b,c]	–

[a] EL-Fadel et al. (1996)

[b] Kim and Somiya (1995)

[c] Yoshikawa (1994)

[d] Somiya (1996)

Table 3 Input values of organics concentrations for simulation

Parameter	Unit	Value
C_{10}	mg C/l	1,785
C_{20}	mg C/l	50
C_{30}	mg C/l	5
C_{r0}	mg C/l	460
C_{T0}	mg C/l	2,300

Steady-state values of each run of the experiments are shown in Table 4. Data from the literature were used as a guide in selecting the values of yield coefficients, self-degradation rate coefficients for acid-forming bacteria, yield coefficients, and membrane passage ratios of degradable solids or polymer organic materials (C_1) and dissolved organic materials (C_2). Based on the experimental results, the rate coefficients k_1, k_2, k_3, and k_d were determined from Eqs. 2, 3, 4, and 6, respectively.

Empirical model for predicting VFA concentrations in effluent

Although many dynamic or steady-state models have been generated to describe anaerobic digestion, few models have considered the kinetics of MCAF-based processes with regard to the recovery of organic materials. No satisfactory model has been developed that evaluates effluent VFA concentrations and the influence of operational parameters sufficiently. Thus, it is necessary to establish empirical relationships based on experimental results.

Wilson (1993) built an empirical model through multiple regression analysis to describe a rotating biological contact system. Simple models that use multiple regression have also been developed for anaerobic filters (Oh and Yang 1986; Yang et al. 1987; Young and McCarty 1969) to predict outlet organic concentrations, substrate loading removal rates, and fractional substrate removal efficiencies. In these models, the hydraulic retention time (HRT) is the sole determinant of the efficiency of organic removal by anaerobic filters.

Table 4 Steady-state values at each run of the MCAF

Parameter	Run 1	Run 2	Run 3	Run 4	Run 5
HRT (h)	8	12	24	48	96
SRT (h)	240	240	240	240	240
Filtration ratio	0.97	0.95	0.9	0.8	0.6
TOC in influent (mg C/l)	1,784	2,159	2,104	2,308	2,510
TOC in reactor (mg C/l)	16,750	14,600	9,710	6,260	5,021
TOC in permeate (mg C/l)	954	1,205	1,110	1,067	1,106
Effluent VFAs (mg C/l)	801	1,097	1,055	910	923
Dissolved organic materials (mg C/l)	12	27	28	21	18

Experimental system and analysis

The system, which had a total working volume of 76 l, consisted of an anaerobic acid fermentor and a ceramic microfiltration (MF) module. A crossflow MF unit (supplied by Nihon Gaishi Co., Japan) with a pore size of 1 μm was used. The crossflow velocity through the membrane module was adjusted by regulating the pump, and the suction pressure was controlled with an outer pump that was attached to the membrane module.

In the raw coagulated sludge in this study, the average concentrations of total solids and volatile solids were 5,600 and 4,300 mg/l, respectively. Carbohydrates were the most predominant organic component, and fiber also constituted a significant proportion of organics. The particle fraction of organic matter was high, as indicated by the ratio of volatile suspended solids to volatile solids, which exceeded 90%.

Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured with a TOC analyzer (TOC-5000, Shimadzu, Kyoto). Permeation flux and membrane filtration ratio, with regard to operation time, were also monitored. VFAs, such as acetate, propionate, butyrate, and lactate, were measured on a gas chromatograph instrument that was equipped with a flame ionization detector (GC-14A, Shimadzu, Kyoto). Measurements of other compounds were made using standard methods (APHA et al. 1998). Gasification and mineralization were calculated using the following equation: [(TOC concentration of input feed sludge (kg C/day) − TOC concentration of membrane permeate (kg C/day)] * 100/TOC concentration of input feed sludge (kg C/day), with the assumption that microbes did not leak through the membrane.

Results and discussion

Model verification

A simulation program was developed for steady-state and non-steady-state values in an MCAF-based process using Eqs. 2 to 7. The results of the simulations are shown in Fig. 2, illustrating the measured and simulated effluent VFA concentrations of the MCAF at each HRT. The experimental results were compared with the numerical outputs from the model—there was reasonably good agreement between the measured data and simulated values. The mathematical model described the performance of the MCAF adequately under the conditions that were investigated.

The MCAF was operated at 5 HRTs (1/3, 1/2, 1, 2, and 4 days) and various membrane filtration ratios (0.6–0.97) to verify the model. Solids retention time (SRT) was maintained at 10 days by controlling the membrane filtration ratio at each HRT. Changes in membrane filtration ratio of the MCAF were made at constant SRTs during all runs in this study—i.e., to determine the recovery efficiencies of VFAs as a function of changes in OLR or HLR, we fixed the SRT using the membrane filtration ratio. The net VFA concentration at HRTs of 8 and 12 h was higher compared with 1 to 4 days.

If the filtration ratio is set to ϕ, the VFA recovery ratio can be expressed as $(C_3 * \phi)/C_{T0}$. $C_{T0} = C_{10} + C_{20} + C_{30} + C_{r0}$. To evaluate the simulation, the VFA recovery ratio was used.

Effect of hydrolysis rate constant (k_1) and organic loading rate (OLR)

The miscellaneous materials in the solids and polymer organic materials in the influent altered the hydrolysis

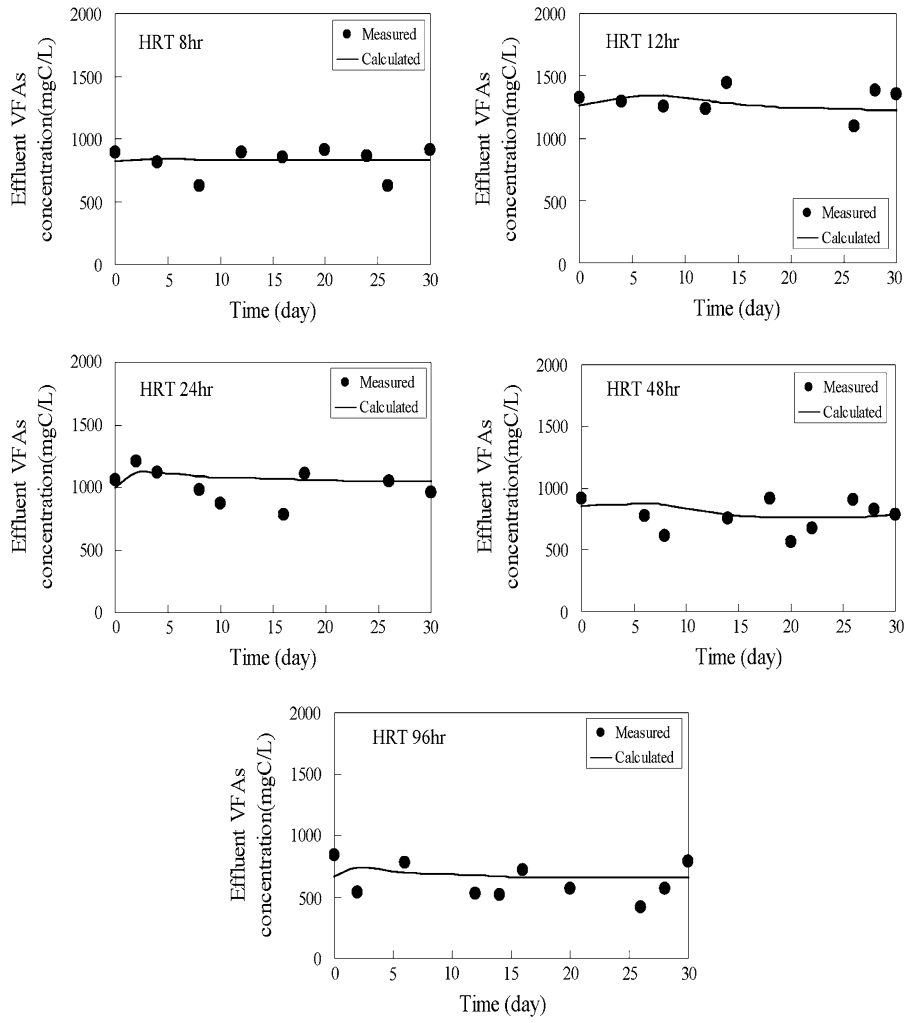

Fig. 2 Measured and simulated VFA concentrations in effluent from the MCAF at each HRT

rate constant. Figure 3 shows the results of the model's simultaneous prediction of variations in hydrolysis rate constant (k_1) and organic loading rate (OLR).

As hydrolysis rate constants modulated over a range of 0.001 to 0.1 (1/h), the VFA recovery ratios were simulated. As under the initial conditions, the HRT of the reactor and the filtration ratio of the membrane were set to 1 day and 0.9, respectively. As shown in Fig. 3, when OLR declined below a certain range, the VFA recovery ratio decreased rapidly. The higher the hydrolysis rate constant was, the greater the effect on VFA recovery ratio was in the OLR range of 0.1 to 1 (kg C/m^3 day). Accordingly, when the hydrolysis rate constant is 0.01 (1/h), the OLR should be maintained above 1.0 (kg C/m^3 day) to attain a VFA recovery ratio of over 40% in the MCAF-based process.

Effect of filtration ratio (ϕ) and refractory material ratio on influent (C_{ro}/C_{T0})

The effect of filtration ratio on VFA recovery ratio is shown in Fig. 4a. At greater filtration ratios, higher VFA recovery and conversion ratios were observed. This result can be attributed to the increase in bacterial concentrations in the reactor by membrane separation. VFA recovery ratio peaked at an HRT of 12 h and a membrane filtration ratio of 0.95 at a constant SRT. When membrane filtration ratio increased at a constant HRT, the microbial concentration in the fermentor increased due to the increases in VFA concentration in the effluent and VFA recovery ratio.

The input TOC concentration, OLR, and HRT of the reactor were set to 2,300 (mg C/l),

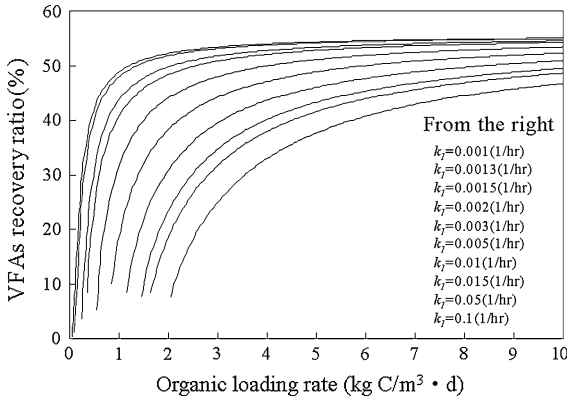

Fig. 3 Effect of hydrolysis rate constant and OLR on VFA recovery

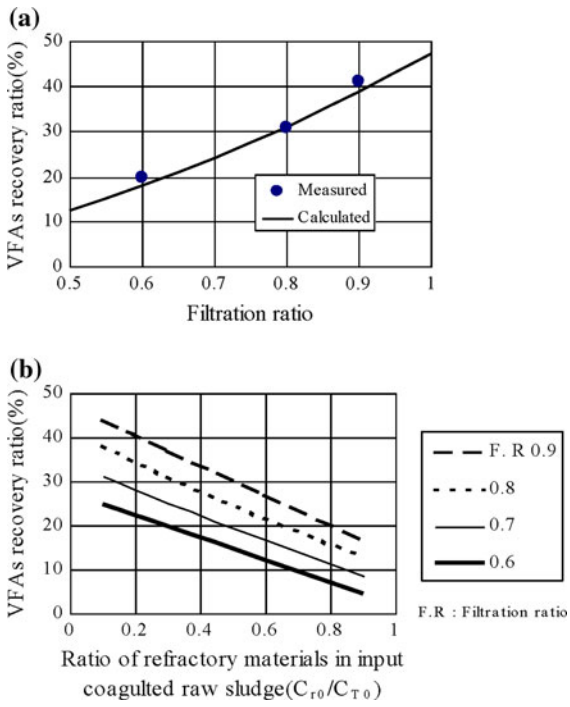

Fig. 4 Relationship **a** between filtration ratio and VFA recovery ratio at constant SRT and **b** between refractory materials ratio of influent and VFA recovery ratio

2.3 (kg C/m^3 day), and 1 day, respectively. Figure 4b shows the effect of refractory material ratios of the influent on VFA recovery ratio.

Based on the simulation results, refractory material ratios in the influent should be an important factor for VFA recovery ratio. We noted that VFA recovery ratios decreased to the same extent as refractory ratios increased. When the refractory ratio was 10% of the influent, the VFA recovery ratio at filtration ratios of 0.6 and 0.9 was 25 and 44%, respectively. The VFA recovery ratio could be increased to 48% as the increase of filtration ratio climbed from 0.6 to 0.9 at a 40% refractory ratio. Therefore, we concluded that the filtration ratio should be maintained above 0.8 to attain a VFA recovery ratio of 30% at refractory ratios below 30%.

Effect of hydraulic retention time (HRT)

Acid phase fermentation products are markedly affected by the specific characteristics of the wastewater; operational parameters, such as HRT and solids retention time (SRT); and environmental factors, such as pH, temperature, reactor configuration, oxidation-reduction potential (ORP), and available trace minerals (Andrews and Pearson 1965; Ghosh et al. 1975).

The HRT is an important operational variable and can be manipulated easily. It governs the amount and type of substrate that is used by bacteria. Because anaerobic digestion is a 2-phase process, HRT acts as a selector in the acidogenic phase only if retention time encourages the growth of acid formers and concurrently suppresses the growth of methane producers.

In this study, the effects of HRT on VFA recovery ratio were examined at an SRT of 10 days by altering filtration ratios and other parameter constants. The input TOC concentration of the coagulated raw sludge was 2,300 (mg C/l), and the refractory ratio of the influent was assumed to be 20%. The HRT was reduced from 4 days (96 h) to 2, 1, 0.5, and 1/3 days for steady-state operation, corresponding to OLRs of 0.6, 1.2, 2.3, 4.6, and 6.9 kg C/m^3 day, respectively. The experimental data are plotted in Fig. 5a to compare the outputs of the mathematical model.

The relationship between mineralization and HRT is shown in Fig. 5b. As shown in Fig. 5, VFA recovery ratios fell as HRT increased, and mineralization rates increased. The VFA recovery ratio was affected by changes in HRT, peaking at 8 and 12 h. The decline at the longest HRT was likely caused by the conversion of soluble VFAs to minerals or gaseous products. Based on these results, we conclude that HRTs and filtration ratios should be maintained at less than 1 day and greater than 0.9 to attain an organic materials recovery ratio of more than 45% at a constant SRT of 10 days.

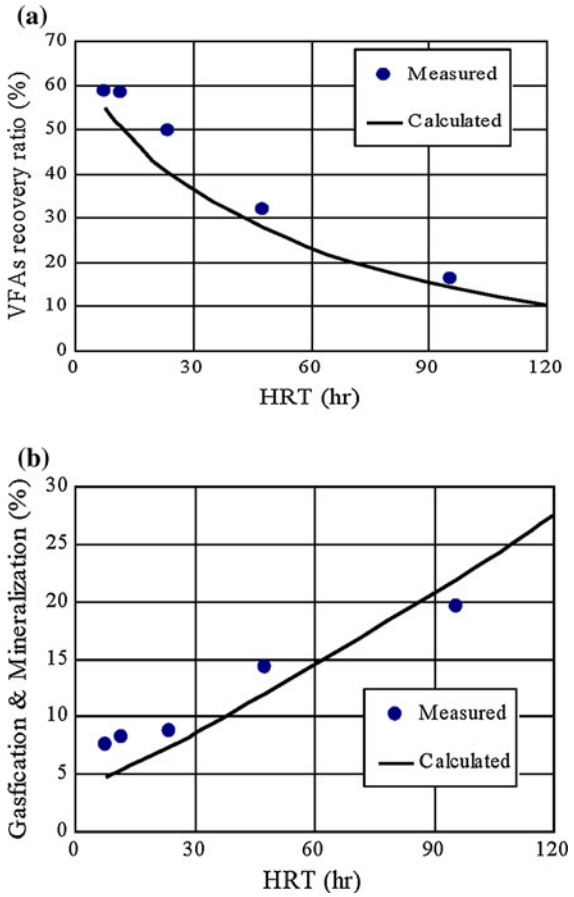

Fig. 5 Relationship **a** between VFA recovery ratio and HRT and **b** between mineralization/gasification rates and HRT

Prediction of effluent VFA concentration by an empirical model

In light of the importance of the influent organic concentration and HLR (or HRT) in determining the effluent VFA concentration, multiple regression analyses were conducted with 50 measurements of the MCAF, generating the following relationships:

$$\ln C_o = 1.93 \ln C_i + 1.13 \ln \phi + 0.11 \ln \mathrm{HLR} - 1.28 \quad (8)$$

Equation 8 can be rewritten to give Eq. 9.

$$C_o = 0.278 \phi^{1.13} C_i^{1.93} \mathrm{HLR}^{0.11} \quad (9)$$

The multiple correlation coefficient (R^2) in Eq. 9 was 0.901. The multiple regression analysis results are shown in Table 5. Based on the high value of R^2, we felt that the relationship in Eq. 9 between ϕ, C_i, and HLR described the performance of the MCAF adequately. The magnitude of the effect of the three operational parameters in predicting the effluent VFA concentration was, in descending order: $C_i > \phi > \mathrm{HLR}$. Plots between the measured and calculated results are shown in Fig. 6.

This figure illustrates that the correlation was good. Our empirical model, which predicted effluent VFA concentrations (C_o), described the performance of the MCAF adequately. Our model demonstrated that the outlet VFA concentration was a function of three independent parameters (HLR, input organic concentration (C_i), and membrane filtration ratio (ϕ)), but it did not account for refractory materials.

The principal purpose of this MCAF-based process was to recover organic materials efficiently, in contrast to most anaerobic treatment processes for methane production, and to verify the validity of our empirical model, other published multiple regression analyses are summarized in Table 6.

As seen in Table 6, with the exception of the study by Dahab (1982), the values of R^2 exceeded 0.85, indicating the validity of the model, despite variations in wastewater properties and media types. Moreover, based on the results of the operational data for the full-scale anaerobic treatment process that was reported by Francis et al. (1998), it appears that the empirical model is applicable in predicting the performance of the process.

From the optimal values of each parameter, we can derive targeted VFA conversion ratios and VFA recovery ratios as actual operational design parameters from the empirical Eq. 9; the optimal parameter values for attaining these ratios are summarized in Table 7. These values were calculated by the maximum-likelihood procedure in Microsoft Excel.

Similarly, controlling the filtration ratio (ϕ) was more effective than the hydraulic loading rate (HLR) in meeting a target VFA conversion ratio. When the conditions of each operational parameter were set, the optimal parameter values were obtained, as shown in Table 7(b) and (c). From the results in Table 7(b), the optimal input organics concentrations (C_i) that satisfied VFA recovery ratios of 30, 40, and 50% were 1,072 (mg C/l), 1,457 (mg C/l), and 1,870 (mg C/l), respectively. Based on these results, due to its simplicity, our empirical model can predict effluent VFA concentrations in membrane-coupled anaerobic fermentation processes.

Table 5 Multiple regression analysis results for the MCAF

Relationship	R^2	Standard Error of Y, ln C_o	Standard error of X, coefficients			Number of measured
			ln C_i	ln ϕ	ln HLR	
$C_o = 0.278\phi^{1.13} C_i^{1.93}$ HLR$^{0.11}$	0.901	0.108	0.117	0.239	0.049	50

C_i: 2,191 ± 237; ϕ: 0.75 ± 0.13; HLR: 2.7 ± 0.1

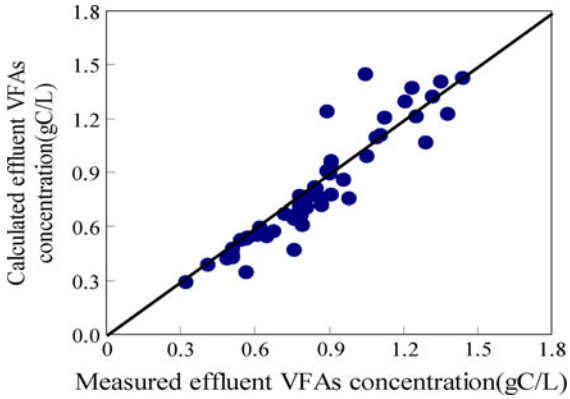

Fig. 6 Measured and calculated VFA concentrations of the MCAF at each HRT

Conclusions

Mathematical and empirical models were developed to determine reliable design conditions of a membrane-coupled anaerobic fermentor (MCAF)-based process and assess its performance. This study was focused primarily on the following points: (1) development of a mathematical model to estimate the appropriate values of operational parameters regarding HRT, OLR, the ratio of refractory material in the influent (C_{ro}), and membrane filtration ratio (ϕ) to determine organic compound recovery and conversion ratios; and (2) establishment of an empirical model, based on multiple regression analysis, to predict effluent VFA concentrations in terms of HLR, C_i, and ϕ. The following noteworthy conclusions were drawn from this study:

(1) Good agreement was obtained between the simulated results of the mathematical model and the measured data.
(2) When OLR declines below a certain range, VFA recovery ratios decrease rapidly. The greater the hydrolysis rate constant is, the greater the effect of VFA recovery ratio is over an OLR range of 0.1 to 1 (kg C/m^3 day). At a hydrolysis rate constant of 0.01 (1/h), the OLR should be maintained above 1.0 (kg C/m^3 day) to attain a VFA recovery ratio of over 40%.
(3) The VFA recovery ratio fell as HRT increased, and mineralization/gasification rate rose. The VFA recovery ratio was affected by changes in HRT, peaking at 8 and 12 h. The decline at the longest HRT was likely caused by the conversion of soluble VFAs to minerals or gaseous products. HRTs and filtration ratios should be maintained at less than 1 day and above 0.9 to attain an organic materials recovery ratio of more than 45% at a constant SRT of 10 days.

Table 6 Multiple regression analysis results from published data on anaerobic treatment

Researcher	Waste type	Media type	OLR (g COD/l day)	Relationship	R^2	Measurement no.
Dahab (1982)	Synthetic (alcohols)	Molecular blocks	0.50–16.00	$S_e = 0.368S_i^{0.73}HRT^{-0.60}$	0.822	26
Oh and Yang (1986)	Synthetic (glucose)	Plastic straw	0.55–5.50	$S_e = 0.148S_i^{1.29}HRT^{-0.47}$	0.867	20
Gonzalez (1987)	Thin stillage	Plastic ring	0.51–21.66	$S_e = 0.276S_i^{1.08}HRT^{-1.32}$	0.940	10
Chiang (1988)	Synthetic (dry milk)	Plastic flexiring	0.98–11.87	$S_e = 0.077S_i^{1.25}HRT^{-0.50}$	0.917	55
Jhung and Choi (1995)	Molasses	Plastic ring	0.75–19.30	$S_e = 6.770S_i^{0.28}HRT^{-0.39}$	0.894	9
Francis et al. (1998)	Soybean wastewater	Fibrous media	4.14–13.29	$S_e = 0.039S_i^{1.48}HRT^{-1.07}$	0.951	233

S_e: organic concentration in effluent (mg C/l)

S_i: organic concentration in influent (mg C/l)

Table 7 The optimal parameter values for meeting (a) a target VFA conversion ratio, (b) a target VFA recovery ratio, and (c) a VFA recovery ratio of 40%

Parameter	VFAs conversion ratio									Parameter condition
	40%			45%			50%			
(a) For meeting a target VFA conversion ratio										
ϕ (–)	0.51	0.29	0.21	0.56	0.32	0.23	0.62	0.35	0.25	$\phi \leqq 0.95$, HLR $\leqq 3$, $C_i \leqq 3{,}000$
C_i (mg C/l)	3,000	6,000	9,000	3,000	6,000	9,000	3,000	6,000	9,000	
HLR (l/l day)	2.67	2.66	2.66	2.67	2.67	2.67	2.82	2.82	2.82	
C_o (mg C/l)	1,200	2,400	3,600	1,350	2,700	4,050	1,500	3,000	4,500	

Parameter	VFAs recovery ratio			Parameter condition
	30%	40%	50%	
(b) For meeting a target VFA recovery ratio				
ϕ (–)	0.95	0.95	0.95	$\phi \leqq 0.95$, HLR $\leqq 3$, $C_i \leqq 3{,}000$
C_i (mg C/l)	1,072	1,457	1,870	
HLR (l/l day)	3	3	3	
C_o (mg C/l)	339	612	991	

Parameter	Value			
(c) For meeting a VFA recovery ratio of 40%				
ϕ (–)	0.95	0.9	0.8	0.7
C_i (mg C/l)	1,457	1,687	2,271	3,347
HLR (l/l day)	3.0	2.5	2.0	1.0
C_o (mg C/l)	612	749	1,136	1,913

(4) The empirical model followed the same trend as the experimental data, which demonstrates the effectiveness of the model. Due to its simplicity, our empirical model can predict effluent VFA concentrations in membrane-coupled anaerobic fermentation processes.

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